Electronic origin of magnetic and orbital ordering in insulating LaMnO$_3$

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We derive a spin-orbital model for insulating LaMnO$_3$ which fulfills the $SU(2)$ symmetry of $S = 2$ spins at Mn^{3+} ions. It includes the complete e_g and t_{2g} superexchange which follows from a realistic Mn^{2+} multiplet structure in cubic site symmetry, and the Jahn-Teller induced orbital interactions. We show that the magnetic ordering observed in LaMnO$_3$ is stabilized by a purely electronic mechanism due to the e_g-superexchange alone, and provide for the first time a quantitative explanation of the observed transition temperature and the anisotropic exchange interactions.

The fascinating properties of doped manganites R$_{1-x}$A$_x$MnO$_3$, where R is a rare earth element, and A is a divalent element, were discovered almost half a century ago [1], but the various phase transitions occurring under doping and in particular the phenomenon of 'colossal magnetoresistance' (CMR) are still not fully understood. The phase diagrams of La$_{1-x}$(Ca,Sr)$_x$MnO$_3$ [2] show a complex interplay between magnetic, charge, and structural order, so that all these ordering phenomena may affect CMR at least indirectly. It is therefore important to obtain first of all a full understanding of the mechanism(s) stabilizing the observed order in the *undoped* insulating parent compound LaMnO$_3$. This will be an essential element in putting together a satisfactory description of the more complicated *doped* compounds, and recognizing which mechanism(s) other than or in addition to double exchange [3] might be responsible for CMR [4].

In this Letter we therefore reconsider the problem of the microscopic origin of the experimentally observed type of antiferromagnetic (AF) order in LaMnO$_3$ [5], which consists of ferromagnetic (FM) planes ordered antiferromagnetically in the third direction (A-AF phase). As the magnetic order in LaMnO$_3$ couples to orbital order [6], one possible explanation might be the occurrence of a cooperative Jahn-Teller (JT) effect [7] which induces a particular order of the singly occupied e_g orbitals [8]. However, while the JT effect plays a crucial role in charge transport [9], we show here that a purely *electronic mechanism* drives orbital and magnetic ordering in the manganites near the Mott-Hubbard transition [10].

The local Coulomb interaction U is the dominating energy scale in late transition metal oxides. If partly filled orbitals are degenerate, as in KCuF$_3$ or in LaMnO$_3$, this leads to an effective low-energy Hamiltonian, where *spin and orbital* degrees of freedom are interrelated [8,11]. In the simplest case of d^9 ions in KCuF$_3$, such a model describes spins $S = 1/2$ of e_g holes coupled to the discrete orbital variables. Finite Hund's rule exchange J_H removes the classical degeneracy of magnetically ordered phases [8,12], and stabilizes the A-AF phase in conjunction with the particular orbital order observed in KCuF$_3$. Here we show that a similar state follows from a *realistic* $S = 2$ *spin-orbital model* for the d^4 ions in LaMnO$_3$. We include also the t_{2g} superexchange and the JT interaction and show that these, while unessential qualitatively, are important for a quantitative understanding.

The *superexchange between total spins* $S = 2$ at the d^4 Mn^{3+} ions originates in the large-U regime from virtual (e_g or t_{2g}) excitations, $d_i^4 d_j^4 \rightleftharpoons d_i^3 d_j^5$. A simplified approach proposed recently by Ishihara *et al.* [13] emphasizes the role of orbitals but violates the $SU(2)$ spin symmetry, and involves a Kondo coupling between e_g and t_{2g} spins, which by itself is not a faithful approximation to the multiplet structure. The latter objection applies also to the model proposed by Shiina *et al.* [14]. In contrast, the spin-orbital model presented below follows from the full multiplet structure of the Mn ions in octahedral symmetry, both in the d^4 ($t_{2g}^3 e_g$) configuration of the Mn^{3+} ground state and in the d^3 and d^5 virtually excited states.

So we consider a spin-orbital model for the manganites,

$$H = H_e + H_t + H_{\mathrm{JT}} + H_\tau, \qquad (1)$$

which includes superexchange terms due to e_g (H_e) and t_{2g} (H_t) excitations, JT interaction (H_{JT}), and a low-symmetry crystal field (H_τ). Our starting point is that each Mn^{3+} (d^4) ion is in the strong-field ($t_{2g}^3 e_g$) Hund's rule ground state, i.e., the high-spin ($S = 2$) orbital doublet ^5E. First, we analyze the strongest channel of superexchange, which originates in the hopping of an e_g electron from site i to its neighbor j. When we consider a bond oriented along the cubic c-axis, only a $3z^2 - r^2$ electron can hop and four d^5 states may be reached: the high-spin $^6A_1$ state ($S = 5/2$), and the lower-spin ($S = 3/2$) $^4A_1$, ^4E, and $^4A_2$ states (Fig. 1). The $d_i^4 d_j^4 \rightleftharpoons d_i^3(t_{2g}^3)d_j^5(t_{2g}^3 e_g^2)$ excitation energies require for

their description in principle *all three* Racah parameters, A, B and C [15]: $\varepsilon(^6A_1) = A - 8B$, $\varepsilon(^4A_1) = A + 2B + 5C$, $\varepsilon(^4E) \simeq A + 6B + 5C$ [16], $\varepsilon(^4A_2) = A + 14B + 7C$. In view of the realistic values of $B = 0.107$ and $C = 0.477$ eV for Mn^{2+} (d^5) ions [17], one may use an approximate relation $C \simeq 4B$, and write the excitation energies in terms of Coulomb, $U \equiv A + 2B + 5C$, and Hund's exchange, $J_H \equiv 2B + C$, parameters: $\varepsilon(^6A_1) = U - 5J_H$, $\varepsilon(^4A_1) = U$, $\varepsilon(^4E) = U + \frac{2}{3}J_H$, $\varepsilon(^4A_2) = U + \frac{10}{3}J_H$. Using the spin algebra (Clebsch-Gordon coefficients) and the reduction of product representations in cubic site symmetry [15] for the intermediate states, and making a rotation of the terms derived for a bond $\langle ij \rangle \parallel c$ with respect to the cubic axes, one finds a compact expression,

$$H_e = \frac{1}{16} \sum_{\langle ij \rangle} \left\{ -\frac{8}{5} \frac{t^2}{\varepsilon(^6A_1)} \left(\vec{S}_i \cdot \vec{S}_j + 6 \right) \mathcal{P}_{\langle ij \rangle}^{\zeta\xi} \right.$$
$$+ \left[\frac{t^2}{\varepsilon(^4E)} + \frac{3}{5} \frac{t^2}{\varepsilon(^4A_1)} \right] \left(\vec{S}_i \cdot \vec{S}_j - 4 \right) \mathcal{P}_{\langle ij \rangle}^{\zeta\xi}$$
$$\left. + \left[\frac{t^2}{\varepsilon(^4E)} + \frac{t^2}{\varepsilon(^4A_2)} \right] \left(\vec{S}_i \cdot \vec{S}_j - 4 \right) \mathcal{P}_{\langle ij \rangle}^{\zeta\zeta} \right\}, \quad (2)$$

where t is the hopping element along the c-axis, and $\mathcal{P}_{\langle ij \rangle}^{\alpha\beta}$ are projection operators for each bond $\langle ij \rangle$,

$$\mathcal{P}_{\langle ij \rangle}^{\zeta\xi} = P_{i\zeta}P_{j\xi} + P_{i\xi}P_{j\zeta}, \qquad \mathcal{P}_{\langle ij \rangle}^{\zeta\zeta} = 2P_{i\zeta}P_{j\zeta}, \quad (3)$$

projecting on the orbital states, being either parallel to the bond direction on one site ($P_{i\zeta} = \frac{1}{2} - \tau_i^\alpha$) and perpendicular on the other ($P_{j\xi} = \frac{1}{2} + \tau_j^\alpha$), or parallel on both sites. They are represented by the orbital operators τ_i^α associated with the three cubic axes ($\alpha = a$, b, or c),

$$\tau_i^{a(b)} = \frac{1}{4}(-\sigma_i^z \pm \sqrt{3}\sigma_i^x), \qquad \tau_i^c = \frac{1}{2}\sigma_i^z, \quad (4)$$

where the σ's are Pauli matrices acting on the orbital pseudo-spins $|x\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $|z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, and the orbitals transform as $|x\rangle \propto x^2 - y^2$ and $|z\rangle \propto (3z^2 - r^2)/\sqrt{3}$.

The spin operators $\vec{S}_i$ in Eq. (2) are $S = 2$ spins, but otherwise H_e resembles the spin-orbital model for d^9 ions in the cuprates [12]. Both models contain superexchange-like couplings between spin and orbital degrees of freedom. The orbital sector carries a discrete cubic symmetry, and is *identical* in both cases, while the *spin problem fulfills the $SU(2)$ symmetry*, and different representations apply for the manganites ($S = 2$) and for the cuprates ($S = 1/2$). We emphasize that the Hamiltonian H_e *is not equivalent* to that of Ref. [13] in any nontrivial limit. A common feature is that FM interactions are enhanced due to the lowest excited $^6A_1$ state, but the dependence of the magnetic interactions on J_H is quite different, and it gives a different answer concerning the stability of the A-AF phase. The balance between AF and FM interactions is also different from that in Ref. [14] due to the multiplet structure of Mn^{2+}.

A similar derivation gives the t_{2g} superexchange [18],

$$H_t = \frac{1}{4}J_t \sum_{\langle ij \rangle} \left(\vec{S}_i \cdot \vec{S}_j - 4 \right), \quad (5)$$

where $J_t = (J_{11} + J_{22} + J_{12} + J_{21})/4$. The exchange elements, $J_{mn} = t_\pi^2 / \varepsilon(^4T_m, ^4T_n)$, where $t_\pi = t/3$ is the hopping between the t_{2g} orbitals, result from local $d_i^4 d_j^4 \rightleftharpoons d_i^5(t_{2g}^4 e_g)d_j^3(t_{2g}^2 e_g)$ excitations within a $\langle ij \rangle$ bond, with energies $\varepsilon(^4T_1, ^4T_1) \simeq U + 8J_H/3$, $\varepsilon(^4T_1, ^4T_2) \simeq U + 2J_H/3$, $\varepsilon(^4T_2, ^4T_1) \simeq U + 4J_H$, $\varepsilon(^4T_2, ^4T_2) \simeq U + 2J_H$, where ^4T_m (^4T_n) stands for the symmetry of d_i^5 (d_j^3) excited configurations, respectively.

The manganite model (1) is completed by the JT term which leads to static distortions and mixes e_g orbitals [7],

$$H_{JT} = \kappa \sum_{\langle ij \rangle} \left(\mathcal{P}_{\langle ij \rangle}^{\zeta\zeta} - 2\mathcal{P}_{\langle ij \rangle}^{\zeta\xi} + \mathcal{P}_{\langle ij \rangle}^{\xi\xi} \right), \quad (6)$$

with $\mathcal{P}_{\langle ij \rangle}^{\xi\xi} = 2P_{i\xi}P_{j\xi}$, and by the tetragonal crystal field,

$$H_\tau = -E_z \sum_i \tau_i^c. \quad (7)$$

The strength of e_g and t_g superexchange can be estimated fairly accurately from the basic electronic parameters for the Mn ion as determined from spectroscopy [17,19] with an estimated accuracy of $\sim 10\%$. We thus use $U = 7.3$ eV and $J_H = 0.69$ eV, and taking into account that the Mn-Mn hopping occurs via the bridging oxygen, $t = 0.41$ eV as follows from $t = t_{pd}^2/\Delta$ with Mn-O hopping $t_{pd} = 1.5$ eV and charge transfer energy $\Delta = 5.5$ eV [20]. This yields $J = t^2/U = 23$ meV and $J_t = 2.1$ meV. The accuracy of these parameters may be appreciated from the resulting prediction for the Néel temperature of $CaMnO_3$, where a similar derivation gives $\hat{H}_t \sim 2\hat{J}_t(\frac{4}{9}\vec{S}_i \cdot \vec{S}_j - 1)$ in terms of Mn^{4+} spins $S = 3/2$ and $\hat{J}_t \approx J_t(1 + J_H/U)$. With our present estimates we obtain $\hat{J}_t = 2.3$ meV and thus $T_N = 124$ K, in excellent agreement with the experimental value $T_N = 110$ K [5].

When considering the manganite (d^4) model (1), it is instructive to treat J_H and E_z as freely variable parameters in order to appreciate the physical consequences of Hund's rule multiplet splitting and orbital degeneracy. The cuprate (d^9) model exhibits symmetry breaking into classical states with simultaneous spin and orbital order [8,12], and similar behavior is expected here [21]. We have considered classical phases with two and four sublattices, and mixed orbitals (MO), $|i\mu\sigma\rangle = \cos\theta_i|ix\sigma\rangle + \sin\theta_i|iz\sigma\rangle$. The mean-field (MF) phase diagram of the e_g-part of model (1), $H = H_e + H_\tau$, at $T = 0$ is similar to that of the cuprate spin-orbital model [12]: at large positive (negative) E_z, one finds AF phases with either $|x\rangle$ (AFxx) or $|z\rangle$ (AFzz) orbitals occupied, while MO phases with orbitals alternating between the sublattices

($\theta_i = \pm\theta$, with $\cos 2\theta < 0$) are favored by increasing J_H. If $E_z < 0$ the spin order is FM (AF) in the (a, b) planes (along the c-axis) in the MOFFA phase, while at $E_z > 0$ two similar phases, MOAFF and MOFAF, are degenerate. For the parameters appropriate for LaMnO$_3$ ($J_H/U \simeq 0.095$) one finds a MOFFA/MOAFF ground state, i.e., *A-AF magnetic order*, while a FM (MOFFF) phase is found only at $J_H/U > 0.12$. The region of stability of the A-AF phase is modified by t_{2g}-superexchange [Fig. 2(a)], but this change is small as $J_t \ll J$. Thus, the observed A-AF magnetic order in LaMnO$_3$ is caused by the *orbital dependence* of the e_g-superexchange and not by competition between FM e_g- and AF t_{2g}-superexchange as proposed in Ref. [13] (where an unrealistically large J_t was used), supporting the qualitative results of Ref. [14].

Although the MF phase diagrams are modified significantly by JT coupling [Fig. 2(b)], the A-AF phase survives around $J_H/U = 0.095$. In fact, the JT interaction (6) by itself enforces alternating orbitals with $\cos 2\theta = 0$, which favors AF spin order, thus stabilizing at small J_H/U the MOAAA phase, promoted further by finite J_t. But at larger J_H/U, even though the JT interaction sets the stage by inducing orbital order as such, the actual magnetic (A-AF) and orbital ($\cos 2\theta \neq 0$) order are *entirely due* to the e_g-superexchange interactions (2).

Finite temperature behavior was investigated in MF approximation, with $\langle\vec{\sigma}\rangle$, $\langle\vec{S}\rangle$, and $\langle\vec{\sigma}\vec{S}\rangle$ constituting independent order parameters [22]. As the largest interaction is in the pure orbital ($\vec{\sigma}$) channel, one may estimate the JT coupling κ from the temperature of the structural transition, $T_s^{exp} \approx 750$ K. The electronic interactions contribute $\simeq 440$ K (Fig. 3), and the rest, $6\kappa \simeq 760$ K, comes from the JT term [23]. Thus $\kappa \simeq 11$ meV, and we have adopted the representative value $\kappa/J = 0.5$. We then calculated the temperatures T_c for the possible magnetic transitions (Fig. 3), taking into account that orbital order with $\cos 2\theta = 0$ already exists below T_s, and calculating selfconsistently the corresponding order parameter $\langle\vec{\sigma}\rangle$ at finite T. The spin order sets in simultaneously with a modification of orbital ordering towards $\cos 2\theta \neq 0$. We find that the preexisting structural transition plays an important role at finite T and reduces the magnetic transition temperature, being otherwise $T_c \simeq J$ [14]. The results are consistent with the phase diagrams at $T = 0$ (Fig. 2), as the magnetic transition corresponds to the same order as found at $T = 0$. For the A-AF (MOFFA) phase we find $T_c \simeq 106$ K [23], in reasonable agreement with the experimental value of 136 K [24].

The magnetic interactions in the A-AF (MOFFA) phase may be found using averages $\langle\mathcal{P}_{\langle ij\rangle}^{\alpha\beta}\rangle$ of the orbital projection operators (3) at $E_z = 0$. They are FM in the (a, b) planes ($J_{(a,b)}$), and AF in the c-direction (J_c) (Fig. 4). Both large J_H/U and $\kappa = 0.5J$ play a decisive role in determining the actual composition of the orbitals, and we find $J_{(a,b)} = -1.15$ and $J_c = 0.88$ meV, somewhat higher than the experimental -0.83 and 0.58 meV [25]. However, their ratio, $J_c/|J_{(a,b)}| = 0.77$, agrees very well with the experimental value of $0.7-0.72$ [25]; in contrast, it would amount to 1.04 for $\kappa = 0$, and to 2.25 if in addition the orbitals were chosen to satisfy $\cos 2\theta = -0.5$.

Summarizing, a coherent overall picture has been obtained for LaMnO$_3$, which is even quantitatively satisfactory. It includes simultaneously the full (e_g and t_{2g}) superexchange and the JT effect, and shows that the orbital dependence of the e_g-superexchange, a *purely electronic mechanism*, is responsible for the observed A-AF order. We emphasize that no fitting of parameters was needed, and the used values of J_H, U, and t, known with an accuracy of $\sim 10\%$, allowed to deduce the value of the JT coupling κ, and gave T_c, $J_{(a,b)}$ and J_c within 30% from the experimental values. We thus believe that Hamiltonian (1) provides a realistic starting point for understanding how the delicate balance of magnetic and orbital interactions in LaMnO$_3$ is affected by doping, leading to a change of magnetic order and to the possible onset of an orbital liquid state [26].

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FIG. 1. Virtual $d_i^4 d_j^4 \rightarrow d_i^3 d_j^5$ excitations which generate effective interactions for a bond $(ij) \parallel c$-axis: (a) for one $|x\rangle$ and one $|z\rangle$ electron, and (b) for two $|z\rangle$ electrons.

FIG. 2. Classical phase diagram of the manganite model (1): (a) no JT effect ($\kappa = 0$), $J_t = 0$ (full lines) and $J_t = 0.092J$ (dashed lines), with the AFxx and AFzz phases separated by a MOAAA phase; (b) including JT effect ($\kappa = 0.5J$), $J_t = 0$ (dashed lines) and $J_t = 0.092J$ (full lines).

FIG. 3. Magnetic transition temperatures T_c ($J = 23$ meV, $E_z = 0$, $J_t = 0.092J$, $\kappa = 0.5J$) for: MOAAA (dashed line), MOFFF (long-dashed line), and MOFFA (full line) phases, and T_s for the structural (MO) phase transition at $\kappa = 0$ (squares). The dotted line indicates realistic $J_H/U = 0.095$.
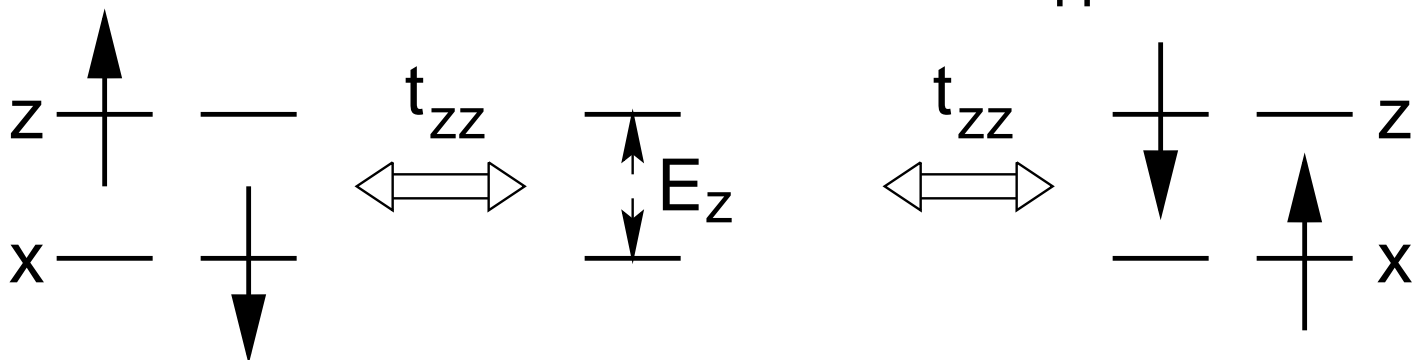
FIG. 4. Exchange interactions J_{ab} and J_c in the ground state for increasing J_H/U, for $J = 23$ meV and: $J_t = 0$, $\kappa = 0$ (dashed lines), $J_t = 0.092J$, $\kappa = 0$ (long-dashed lines), and $J_t = 0.092J$, $\kappa = 0.5J$ (full lines). The inset shows $\cos 2\theta$.

(a)

$^4E_\theta$ — $U + \frac{2}{3}J_H$

$^4A_1$ — U

$^6A_1$ — $U - 5J_H$

z — t_{zz} — E_z — t_{zz} — z

x — x

(b)

$^4A_2$ — $U + \frac{10}{3}J_H$

$^4E_\varepsilon$ — $U + \frac{2}{3}J_H$

z — t_{zz} — t_{zz} — z

x — x

d_i^4 d_j^4 — d_i^3 d_j^5 — d_i^4 d_j^4